SELF-DISINFECTION AND DECONTAMINATING INTERIOR SURFACES BASED ON PHOTOCATALYTIC TITANIA/EASY-RELEASE COATINGS

Robert E. Baier
Biomaterials Graduate Program, University at Buffalo, Buffalo, NY 14214
Christopher M. Izzo
Harmac Industries, Buffalo, NY 14215
Paul J. Nicotera
Rensselaer Polytechnic Institute, Troy, NY 12180

ABSTRACT

We have demonstrated that easy-release qualities imparted by thin methyl-terminated silane coatings, when combined with catalytic disinfection by titanium dioxide particles embedded in or superficially attached to duct-liner fiberglass surfaces and coated fiberglass-based architectural fabrics, can improve the sanitary performance of HVAC air-handling systems. This project evaluated the application of such coatings/particles to duct-wall fiberglass surfaces and coated fibrous glass compositions. The surface-modified materials were placed in a HEPA-filtered laboratory air-duct system, infused with calibrated bioaerosols and sampled with surface science methods sufficiently sensitive to determine the additives' efficacies with regard to discouraging bacterial colonization and habitation. Photocatalytic disinfecting and self-cleaning activity, induced by exposure to "black light" (UV-A) illumination, was followed by spectrometry of methylene blue solution bleaching, as well as by infrared and bacterial culture techniques.

INTRODUCTION

It has previously been demonstrated and confirmed[1,2] that air can be disinfected by photocatalytic techniques similar to those proved to be successful in killing microorganisms in water[3,4,5]. The specific scientific details, most relating to the reaction chemistry of titanium oxides, are published in a 1997 review[6].

Regarding the goal of sanitizing and keeping potentially infected contact surfaces of interior building surfaces clean, one of the main differences from underwater systems for reliable and repeatable disinfection is that dead or destroyed microbes are not as easily washed off the ducts' or building envelopes' antimicrobial surfaces. Thus, an additional probable improvement in building and duct-liner properties would be to make the liners less retentive of particulate debris. This has been accomplished earlier with underwater easy-release coatings[7] and now the same concept is newly extended to serve as the surrounding easy-release matrix for photocatalytic titanium dioxide particles.

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Many indoor air quality problems have been associated with bioaerosols of more than 60 different types. These include mainly bacteria, viruses, and fungi that can cause tuberculosis, Legionnaires' disease, flu outbreaks, mumps, measles, pneumonia, and meningitis, as well as increasing incidences of asthma, upper respiratory distress syndromes, and the common cold[8,9,10]. It has been a difficult problem to study the influences of various possible infection control techniques in HVAC systems and other building structural spaces because of the presence of complex backgrounds of occupant- and furnishings-generated aerosols in most interior work environments and because of the absence of controlled, safe sources of representative bioaerosols.

We recently have produced and calibrated a reliable bioaerosol generating technique[11] and utilized the so-generated aerosols to test bioaerosol-collection equipment at the end of a HEPA-filtered air-duct system that is more versatile than "clean room" test environments previously described[12].

Thus, we have now completed several series of tests of combinations of titanium dioxide photocatalysts and fouling-release coatings in air-ducts lined with fibrous glass blankets, rigid fibrous glass duct board, and other potential building envelope interior linings.

Most prior uses of titanium oxide photocatalysts have required illumination of the oxide particles with ultraviolet [UV] light, to produce the highly reactive free radical species that not only can disinfect an air stream but also break down volatile organic compounds for odor control[13,14]. We have used UV sources, and also explored the use of miniscule amounts of coating additives/amendments and other special treatments that might allow these processes to take place in the dark or under only modest, visible-light illumination. The experimental program monitored (1) the proportions of standardized bioaerosol colony-forming-units [CFU] that were collected and inactivated by the various coating surfaces, (2) the levels of surface-cleanliness maintained over long operating times in continuously operated air-duct systems, and (3) the collectibility and viability of microorganisms advected through ducts and/or admixed with TiO_2 powder at various atmospheric conditions [dry v. humid; "sunlight" illuminated v. dark]. We believe the results can lead to suitable manufacturing applications as pre-coated systems for building interiors that can be cut and fabricated according to current procedures, with current tools.

The experimental techniques employed so far included internal reflection infrared spectroscopy, UV and visible light spectrometry, critical surface tension analysis, scanning electron microscopy and energy dispersive x-ray analysis, as well as air-impaction/collection techniques and standard plate-counting microbial methods for active CFU. A follow-up study now in progress is addressing the basic scientific issues about the mechanisms of reaction. One prospect to be considered is that the titanium dioxide free radical is uniquely produced[15], rather than the ubiquitously generated hydroxy and superoxide-anion free radicals thought to degrade pesticides[16] and phenolic pollutants (especially in the presence of silica)[17], formaldehyde, and trichloroethylene[18]. Of special interest to ongoing research is further exploration of the finding that some titanium dioxide coatings are both self-cleaning and anti-fogging, as ultraviolet radiation converts them from initially hydrophobic to "amphiphilic" surfaces[19]. It is generally agreed that titanium dioxide coatings can be a suitable approach for mass building envelope use, since they are nontoxic, extremely stable, function at normal room temperatures, and inexpensive to manufacture[20,21]. Indeed, there is growing use of titanium (oxide) foil in the food processing industry[22].

MATERIALS AND METHODS

A supply of titanium dioxide (P25) powder was obtained from Degussa Corporation, and commercially pure titanium foil as prepared for food processing equipment from IBR Corporation[22]. New, custom-fitted ductwork was constructed (Capital Heat, Inc., Depew, NY) and installed adjacent to the

laboratory Class 100 Clean Room. The duct received HEPA-filtered, constant- temperature, constant-humidity air exiting from the Clean Room. The air flowed at controlled velocities of 1-2 meters per second [2-5 miles per hour], at static positive pressure of about 3mm [one-eighth of an inch] of water, through removable test duct sections at a volume flow rate of about 240 cubic feet per minute [about 9 cubic meters per minute]. The emerging flow, after having received calibrated aerosol injections and exposures to control techniques, passed into various analytical devices prior to exiting through a continuously operating chemical fume hood. There was great versatility to this test system, which is currently being further instrumented to allow video microscopy of events internal to and at the walls of the modified ducts [Figure 1].

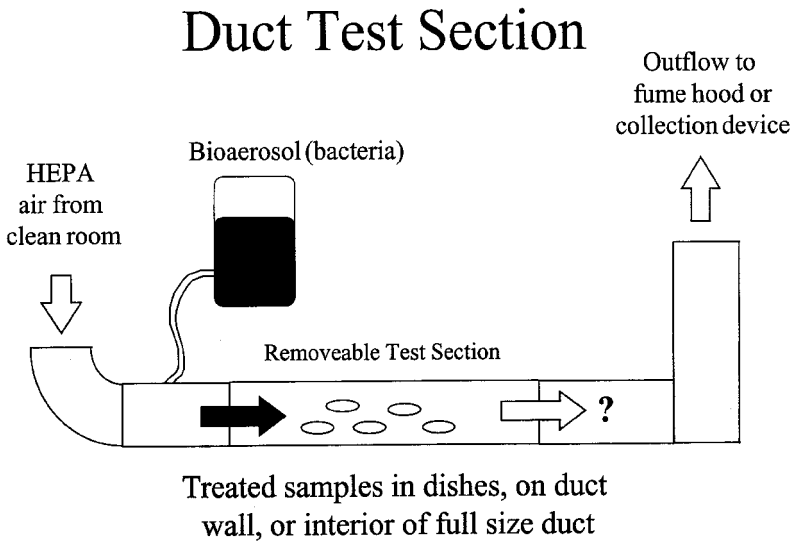

Figure 1. Schematic diagram of the laboratory test apparatus.

Numerous ultraviolet and visible illumination sources were used as required to photoactivate the titanium dioxide powder and, based on significant prior work in the development of fouling-release coatings[23], supplies of coating reagents were obtained from Petrarch Division of United Chemical Technologies, Inc. Specialized equipment for glow-discharge-activation and disinfection of the various test surfaces[24] was used for test specimen pre-cleaning and sterilization, and for conversion of TiO_2 coatings to "visible-light-activatable" status. Custom-built equipment for source assessment of atmospheric aerosols was used routinely[25]. CertainTeed Corporation (Blue Bell, PA) supplied fibrous glass insulation blanket and duct board materials to initiate work, and architectural membranes were supplied by BIRDAIR, Inc. (Amherst, NY).

The analytical methods used are described below:

Internal Reflection Infrared Spectroscopy was applied to confirm the chemical composition of test surfaces (e.g. insulation tissues, coating materials) and to confirm that coatings were, indeed, present on the interior building materials. Infrared spectroscopy detects covalently-bound moieties (e.g. hydroxyl, hydrocarbon, amide, silica, silicone, phosphate) present in a sample. Use of the multiple-attenuated internal reflection mode of IR spectroscopy enables analysis of the outermost 1000 Angstroms,

approximately, of the sample surface, eliminating interfering signals from the sample bulk. Test samples are spread on or clamped against internal reflection test plates (germanium or salt blends that allow for transmission of IR energy), which serve as "lightpipes" for IR energy. While the maximum thickness sampled by this ambient-environment technique is 1000 Angstroms, the minimum detection limit is one monolayer (approximately 15 Angstroms). Other surface spectroscopies (e.g. Xray photoelectron spectroscopy [XPS or "ESCA"] or secondary ion mass spectrometry) are more surface-specific (evaluating only the outermost 15-50 Angstroms of a material) than internal reflection IR spectroscopy, but work only under ultra-high vacuum environments. The efficacy of UHV spectroscopies also tends to be hampered by irregular surface textures, such as the fine fibrous geometries presented by insulation materials. UHV spectroscopic techniques were available to this project, however, and used as necessary to evaluate model films of coating materials.

Critical Surface Tension Analysis, or "comprehensive contact angle analysis" was the most surface-specific physical/chemical technique utilized, probing the outermost 5-10 Angstroms of test materials. Surface descriptors determined from measurements of contact angles of each of up to 15 diagnostic fluids included (a) critical surface tension - indicated overall material "wettability" and dominant chemical functionality at the solid surface, and predicted the relative bioadhesive strength of macromolecules and cells that might attach to the material surface) and (b) surface free energy and its various components – measured the total "potential" for a material to interact with its environment (e.g. extremely clean glass is a high-energy material; "Teflon" is a very-low-energy material); surface energy components included the dispersion force and polar force; polar forces were defined and calculated according to several different theories.

Scanning Electron Microscopy and Energy-Dispersive Xray Analysis were used to confirm surface morphology (SEM) and general elemental composition (EDXray), as well as to visualize the presence of microorganisms and other particulates that collected on the treated and control interior surfaces.

Air Impaction Techniques included the use of customized air-sampling units that deposit particulates from the sampled air onto either germanium internal reflection plates (for subsequent IR spectroscopic and SEM/EDXray analyses) or culture plates (for detection/enumeration of microorganisms in the airstream).

Microbial Culture Techniques were used to detect microorganisms present in the airstream (as described above), and to detect/enumerate cells present on the treated and control insulation surfaces; both agar- and broth-based culture methods were evaluated. Lacking reliable means to quantitatively remove cells from the test surfaces (e.g. washing and/or sonication failed in this regard), the numbers of viable organisms present after different exposure periods were determined by direct placement of the test specimens on nutrient agar surfaces and followed for several days of incubation.

RESULTS

Numerous experiments were executed in accord with the typical experimental plan diagrammed in Figure 2. A parallel series of experiments was done with replicate specimens immersed in methylene blue solutions (rather than being exposed to bacterial "seeding"), and the UVA-induced bleaching of the solutions was followed quantitatively by UV/visible spectroscopy. The spectroscopic results correlated well with the bacterial growth observations.

Due to the visual and somewhat subjective nature of the bacterial growth observations, photo-documentation was employed to record the results of placing samples on agar culture plates. These photos were printed and archived as color slides.

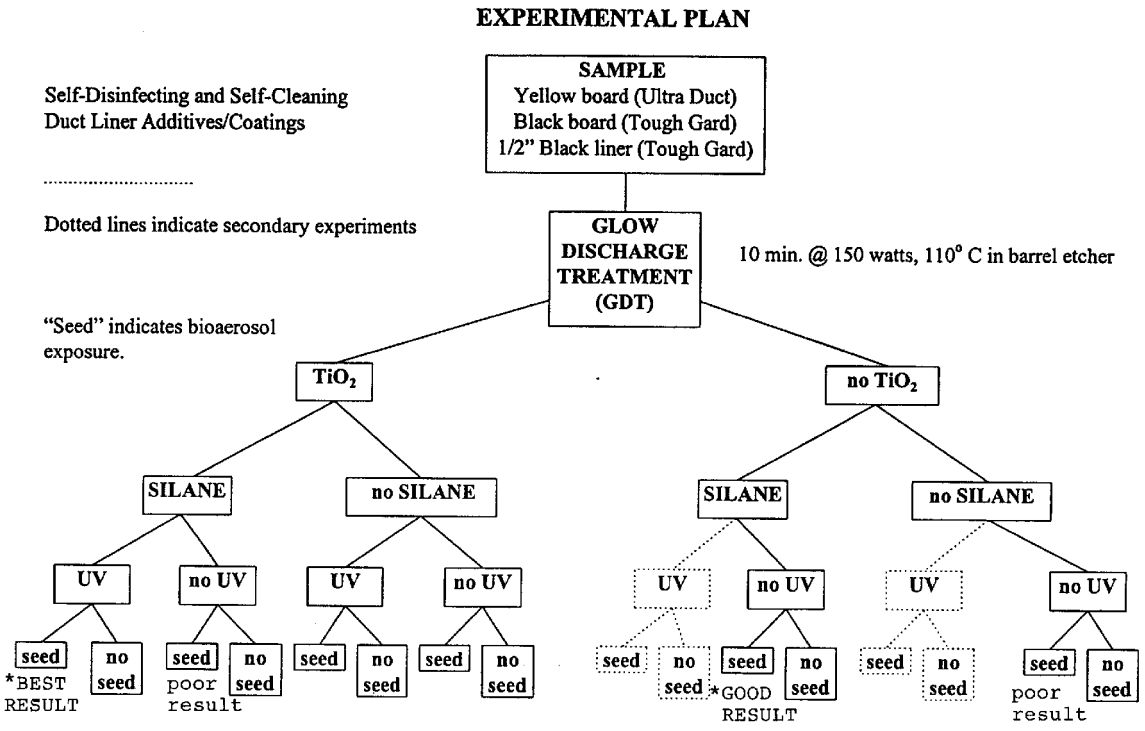

Figure 2. A typical experimental plan, leading to final results noted by asterisk [*] on diagram above. Experimental variations included substituting standard steam autoclaving for the glow discharge treatment [GDT] sterilizing step. The best-performing easy-release coating was octadecyl silane.

Baseline analysis showed clear morphological and chemical differences among interior surface and insulation types and confirmed the ability of glow-discharge treatment to change the surface chemistry sufficiently to make the fiberglass accepting of further modification by easy-release coatings. Particle-amended insulation surfaces without UV-A illumination showed little evidence of antibacterial action and, in fact, showed a greater rate and extent of bacterial growth than unmodified insulation types. Differences in propensity for bacterial growth were observed among insulation and fabric types, as well as between as-received and glow-discharge-treated [GDT] samples, with the GDT specimens usually being sterile.

Titanium dioxide suspension coating at low concentrations gave observable and measurable coating of fibers, as evidenced by SEM and x-ray analysis, and good photocatalytic action was displayed by these materials when illuminated by standard "blacklights" (UV-A). Silane coatings were readily concurrently imparted to insulation samples and further changed the surface chemistry, providing an easy-release, as well as a strong hydrophobic character to samples.

The presence or absence of biology on test samples was viewed most readily by culturing out on agar plates, followed by photo-documentation and visual analysis. Titanium dioxide-containing samples, exposed to UV-A light, sometimes showed a delayed action in the attenuating of bacterial growth on agar plates. That is, despite an initial outgrowth of biology that was just as robust as that of untreated samples, there was a visible reduction in vigor and rate of that growth in the days following the initial seeding experiment.

Work in Progress: A setup for parallel flow IR analysis is being implemented for more sensitive examination of the mechanisms involved in disinfection at the interior surfaces. This involves passing the air flow over germanium and silicon plates in place in a spectrophotometer so that real-time measurements can be made during introduction of bacteria, illumination by UV light, and with the passage of time. Parallel flow will be achieved by constructing an alternative air passage that fits within the physical confines of a dedicated infrared spectrophotometer and horizontal testplate holder. Appropriately coated germanium plates duplicate the surfaces of modified and unmodified fiberglass insulation and architectural membranes, and will facilitate a closer look at the surface chemistry involved in the disinfection processes. In addition to providing a better understanding of the work being performed, this method of examination provides the basis for student thesis work (C. Izzo, M.S. candidate).

CONCLUSIONS

Photocatalytic titanium dioxide (TiO_2) fine particles and easy-release, low-critical-surface-tension (CST) coatings have been shown to be independently capable, respectively, of diminishing viability and minimizing bioburdens on interior surfaces. Unique combinations of TiO_2 and methyl-terminated [CST = 22 mN/m] monolayer coatings on germanium, silicon, fiberglass, and coated fiberglass substrata have been tested in controlled flows of a "zero" air-duct system emerging from a Class 100 clean room, seeded midway to a final exit hood from a controlled bioaerosol generator, and monitored by a new Computer Optimized Aerosol Sampling Technique (COAST II)[26]. Data from cultures for generated versus final colony-forming units, supported by internal reflection infrared spectra, scanning electron micrographs, and energy-dispersive x-ray spectra, show that both active bacterial bioburdens and total retained biomass can be significantly reduced by these surface modifications. Interior surface coatings of TiO_2/easy-release adducts, particularly on fiberglass and coated fiberglass substrata, can substantially aid in maintaining and improving air quality in biologically challenged closed spaces.

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